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HOWARD UNIV WASHINGTON D C DEPT OF CHEMISTRY  
RAMAN SPECTRUM OF PRESSURE COMPACTED FUSED SILICA. (U)

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JAN 81 G E WALRAFEN, P N KRISHNAN

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↑ Raman Spectra have been obtained from fused silica irreversibly  
compacted at 90 kbar. Slight spectral sharpening was observed  
similar to that seen in Raman studies of neutron densified fused silica.

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by

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P. N. Krishnan

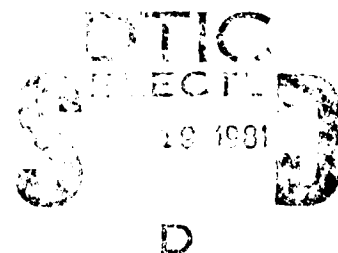
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"Raman Spectrum of Pressure Compacted  
Fused Silica"

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(2)

In 1953 Bridgman and Simon<sup>(1)</sup> produced an irreversibly compacted modification of fused silica. By applying pressures of 10 GPa (100 kbar) at room temperature, a vitreous material was produced that lacked an x-ray diffraction pattern and had a density of  $2.6 \text{ g cm}^{-3}$  (2) MacKenzie<sup>(3)</sup> later obtained infrared spectra of compacted fused silica, but only slight changes in the Si-O stretching frequency were uncovered. Raman spectra of compacted fused silica, however, do not appear to be available, despite the fact that such spectra may be obtained at 1 atm. Accordingly, the Raman spectrum from compacted fused silica was obtained in this work, Fig. 1.

The compacted glass studied here was prepared by W. A. Rocco in R. H. Wentorf's laboratory<sup>(4)</sup> by subjecting ordinary fused silica to a pressure of 9.0 GPa for 1 h at 23°C. Densities of the uncompacted glass,  $2.22 \text{ g cm}^{-3}$  and of the compacted disk,  $2.40 \text{ g cm}^{-3}$  cut from the parent rod, were determined using buoyancy methods. The densified glass disk was about 1 mm thick and 6 mm in diameter. It had an irregular layered appearance, but it was sufficiently stable to be mounted, and it readily transmitted 514.5 nm laser light.

Raman spectra were obtained from the compacted disk and the uncompacted rod under identical conditions, e.g., laser power, amplifier gain, slit width ( $5 \text{ cm}^{-1}$ ), sample positioning, and polarization,  $z(x \frac{x}{y})y$ , Fig. 1, etc. The argon ion laser beam was transmitted radially through the disk or rod, and the Raman radiation was collected along the rod axis.

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The irregular layered nature of the sample produced severe laser light scattering, however, which greatly increased the stray light in the Instruments S. A. HG2S double monochromator. An unavoidably large baseline curvature resulted, upper spectrum, Fig. 1.

The Raman spectrum of the compacted glass disk (compacted) is compared to that from the uncompacted parent rod (normal) in Fig. 1. The gross spectral features of the two samples are very similar--no significant frequency changes of the Si-O stretching bands at 1060 and 1200  $\text{cm}^{-1}$  are apparent, cf., Ref. (3). However, careful analysis of the low-frequency Raman region including comparisons employing baselines A, B, and C (upper spectrum),<sup>(5)</sup> indicates that: (1) the intense Raman feature nominally at 440  $\text{cm}^{-1}$  narrowed with compaction by about 18  $\text{cm}^{-1}$  from a FWHH value of 278  $\text{cm}^{-1}$  (normal), to 260  $\text{cm}^{-1}$  (compacted), (2) a general loss of intensity primarily to the low-frequency side of the 440  $\text{cm}^{-1}$  peak occurred,<sup>(5)</sup> (3) the weak shoulder on the 440  $\text{cm}^{-1}$  peak at about 350-375  $\text{cm}^{-1}$  weakened,<sup>(5)</sup> and (4) the 440  $\text{cm}^{-1}$  peak shifted upward in frequency from  $432 \pm 2 \text{ cm}^{-1}$  (normal), to  $441 \pm 2 \text{ cm}^{-1}$  (compacted), a change of 5 - 13  $\text{cm}^{-1}$  (It would also appear that a weak broad feature at 900  $\text{cm}^{-1}$  occurring as a foot on the 800  $\text{cm}^{-1}$  Raman peak from normal fused silica, is more appropriately described as a weak separate maximum in all of the present compacted spectra.) Stolen et al.<sup>(7)</sup> and Bates et al.<sup>(8)</sup> observed a narrowing and loss of low-frequency intensity below 440  $\text{cm}^{-1}$  in the Raman spectrum of neutron compacted fused silica, see Ref. (7) Fig. 1. An upward

(4)

shift of the  $440\text{ cm}^{-1}$  peak position,<sup>(7,8)</sup> and a strong intensification of the  $603\text{-}609\text{ cm}^{-1}$  defect peak were evident.<sup>(7,8)</sup> Also, a slight change at  $900\text{ cm}^{-1}$  similar to that observed here was indicated,<sup>(8)</sup> and a  $10\text{ cm}^{-1}$  increase in the  $800\text{ cm}^{-1}$  peak position was related to an angular decrease of  $4^\circ$  in the mean Si-O-Si bridging angle.<sup>(7)</sup>

Raman observations of Refs. (7,8) are similar to ours, except that no obvious intensity changes occurred for either of the defect peaks at  $604$  and  $490\text{ cm}^{-1}$ .<sup>(9)</sup> Raman spectral effects of pressure compaction are phenomenologically similar (although weaker) to those of neutron compaction for some specific features of the main glass network, but dissimilar for defects. Broken bonds are known to exist in neutron compacted silica,<sup>(10)</sup> however, and these may indirectly increase the defect concentration and thus the  $604\text{ cm}^{-1}$  intensity. But broken bond and/or defect concentration changes do not seem to be compatible with the present results. Further, we see virtually no change in the  $800\text{ cm}^{-1}$  peak position, although some slight shape changes may exist between  $750\text{-}950\text{ cm}^{-1}$ .

In conclusion, pressure compaction produces some changes in the network structure of vitreous silica, but no sizeable changes in the defect structures. Defect concentrations, and hence defect intensities at  $604$  and  $490\text{ cm}^{-1}$  are increased by increases in the fictive temperature,<sup>(9)</sup> but apparently not by irreversible compaction.<sup>(11)</sup> We also are reluctant to infer sizeable changes in the mean Si-O-Si bridging angle, or the mean Si-O bond length, although changes in the  $\text{SiO}_4$  structures, or in the mean torsional angle between  $\text{SiO}_4$  tetrahedra, are not ruled out.

(5)

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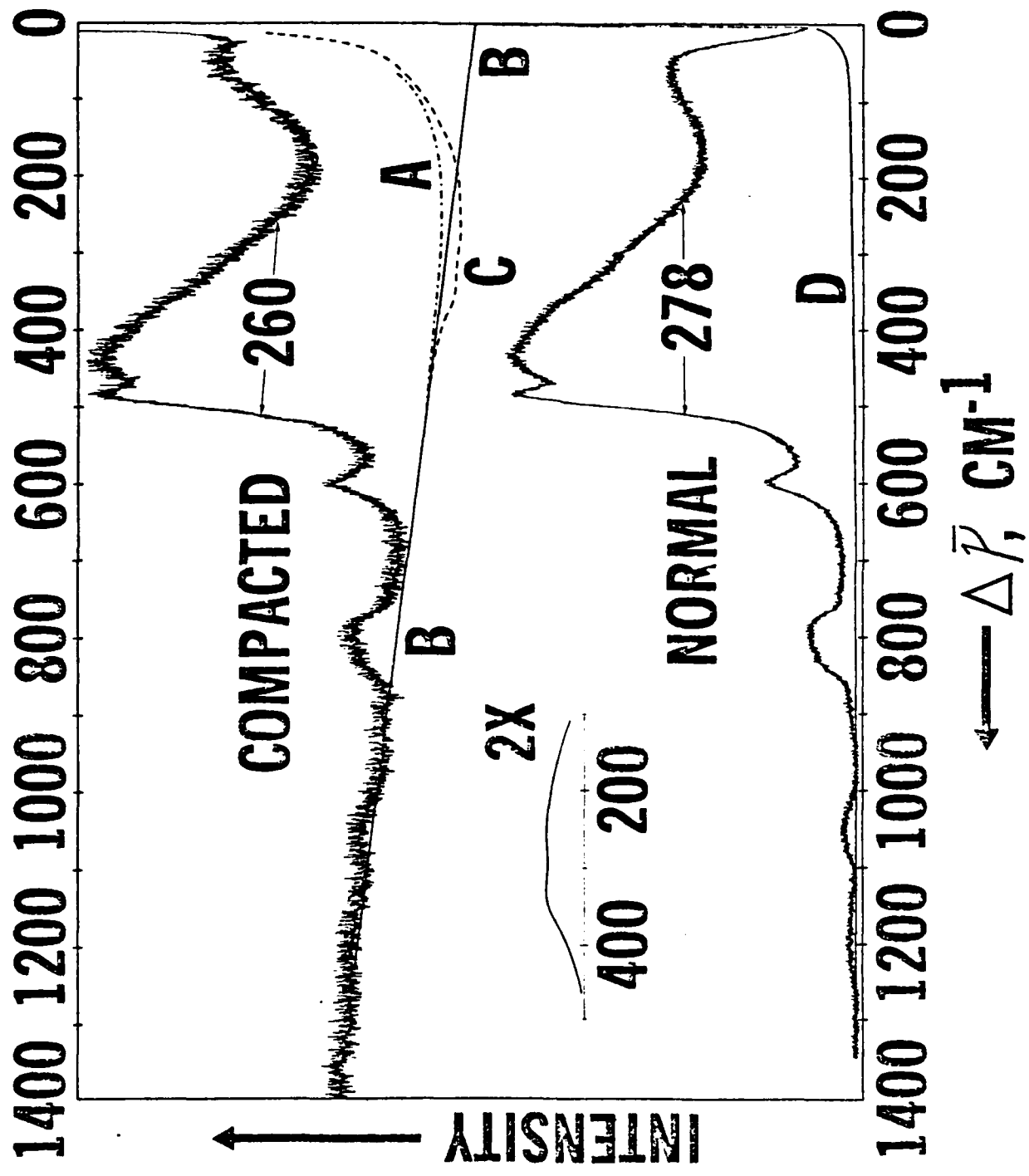
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2. Density of fused silica, about  $2.2 \text{ g cm}^{-3}$  quartz, about  $2.65 \text{ g cm}^{-3}$
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4. General Electric Research Laboratory, Schenectady, NY.
5. To compare the two spectra of Fig. 1 it was necessary to normalize them using amplitudes of three peaks between  $440$  and  $604 \text{ cm}^{-1}$  to determine if differences occurred elsewhere. From peak height ratios at  $604$ ,  $490$ , and  $440 \text{ cm}^{-1}$  above baselines A and D, Fig. 1, and from ratios of vertical height differences between the  $604$  and  $490 \text{ cm}^{-1}$  peaks, the scattering level of the uncompact spectrum was determined to be 1.04 times greater than that of the compacted spectrum. The uncompact Raman intensities from  $0$ - $1400 \text{ cm}^{-1}$  were then divided by 1.04 and subtracted from the corresponding compacted spectral intensities. This procedure yielded baseline C, which represents the baseline that the compacted sample would have, if no spectral effects had occurred. However, baseline C falls below baselines B and A at low frequencies, thus definitely indicating spectral changes. Baseline B, the straight sloping baseline, constitutes the low baseline limit at low Raman frequencies. Baseline B resulted from linear extrapolation of a small fluorescence contribution at the larger Raman frequencies.<sup>(6)</sup> Baseline A, above baseline B, is a realistic estimate. The difference between baselines A and C is a measure of the spectral changes, conclusions (2) and (3). Twice this difference is shown in Fig. 1 between  $100$ - $500 \text{ cm}^{-1}$

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CAPTION

Figure 1. Raman spectrum of compacted vitreous silica (upper) and of normal fused silica (lower). A and D are realistic baseline estimates. B is a low baseline limit at low frequencies. Baseline C was obtained by subtracting the uncompacted intensity/1.04, from the compacted intensity. For clarity, the differences between baselines A and C were multiplied by 2, inset to left. This difference is a spectral measure of some effects of compaction. Values on arrows are full width at half height (FWHH) in  $\text{cm}^{-1}$ . Arrows are approximately parallel to baselines A and D.



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